# MEASUREMENT AND PREDICTION OF PHASE EQUILIBRIA FOR WATER+METHANE IN HYDRATE FORMING CONDITIONS[1]

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**ABSTRACT**

Clathrate hydrate of methane became of importance as an energy resource and as a problem to natural gas industry. Data are available for various phase equilibria, but methane solubility in $H$-$L_W$ equilibria was not reported. In this study methane solubility were measured in the pressure range from 2 to 20 MPa and in the temperature range of 273-285K. Applicability of the lattice fluid equation of state by present authors was also investigated for the unified description of various phase equilibria. With Langmuir constants in the van der Waals and Platteeuw model for hydrates and hydrogen-bonding free energy of water fitted to data, the model was found to consistently describe various two and three phase equilibria of $L_W$-$V_{CH4}$, $H$-$L_W$-$V_{CH4}$, $H$-$I$-$V_{CH4}$, $H$-$L_W$, and $H$-$V_{CH4}$. With a single binary interaction parameter, good agreements between observed and calculated results were obtained except for water contents in methane-rich phase of $L_W$-$V_{CH4}$ equilibria where the error becomes larger.

Keywords: equation of state; experimental method; gas hydrate; methane; vapor-liquid equilibria; water

**INTRODUCTON**

Since the early nineteenth century, water molecules have been known to form clathrate hydrates when stabilized by guest molecules occupying cavities in the crystal even above the freezing point of water. After a period of scientific interest clathrate hydrates became important as an energy resource and as a problem to natural gas industry. The history and the recent status of clathrate hydrate research are well documented in Sloan, Jr.'s book [1].

Hydrate-methane-water systems involve various phases; namely, hydrate (H), water-rich liquid ($L_W$), methane-rich vapor ($V_{CH4}$) and ice (I). Most studies of gas hydrate have concentrated upon measuring the three-phase dissociation pressure. However, few data are available for H-$L_W$ phase equilibria. This may be important for practical applications and developing thermodynamic models. For equilibrium calculations, an equation of state and a set of parameters can describe all fluid phase, in principle. Authors recently proposed a unified approach for various phase equilibria involving water, carbon dioxide and hydrate [2].

In the present study H-$L_W$ equilibria are to be experimentally studied for methane hydrate-water system. Applicability of lattice-fluid equation of You et al. [3, 4] and its extension to associating system [5, 6] for a unified description of these equilibria is to be investigated.


**THEORY**

Various phase equilibria may be calculated once chemical potentials or fugacities of components for different phases are calculated. For fluid phases, they may be obtained using an appropriate equation of state (EOS). The EOS approach is advantageous for

systems involving hydrates that are formed at high pressures. In a theory based on partition functions, chemical potential is conveniently evaluated and is used extensively instead of fugacity.

We write the two-phase equilibrium relation involving hydrate phase. For water,

$$\mu_W^\Pi = \mu_W^H \qquad (1)$$

where $\Pi$ denotes liquid or vapor. The chemical potential of a component $i$ in a fluid phase ($\Pi$) is readily written from the work of You et al. [3, 4] and Lee et al. [5, 6] for associating as well as non-associating systems.

The expression for chemical potential of water in hydrates is based on van der Waals and Platteeuw model [1].

$$\mu_W^H = \mu_W^{EH} + RT\sum_j v_j \, ln[ \, 1 - C_{i,j} f_i^\Pi \, /( \, 1 + C_{i,j} f_i^\Pi \, )] \qquad (2)$$

where $j$ denotes cavities which guest molecules can occupy, $\Pi$ denotes a fluid phase, $\mu_W^{EH}$ is the chemical potential of empty hydrates, $v_j$ is the number of cavities of type $j$ per water molecule in the hydrate lattice ($v_1 = 1/23$ and $v_2 = 3/23$), $C_{i,j}$ is the Langmuir constant for each kind of cavities. An intermolecular potential was used to calculate the Langmuir constants in many previous studies. However this complex approach does not eliminate the necessity for adjustable intermolecular potential parameters. Nagata and Kobayashi [7] showed that Langmuir constants can be approximately represented by,

$$C_{i,j} = \exp(A_{i,j} + B_{i,j} \times T) \qquad (3)$$

Langmuir constants can be regressed from three-phase equilibrium data. Spectroscopic studies showed that only gases of modest size and of appropriate geometry could occupy the cavities. The fugacity of component $i$ in eqn (2) is calculated from the chemical potential,

$$f_i^{\Pi} = P^0 \exp[(\mu_i^{\Pi} - \mu_i^{\Pi 0})/RT] \tag{4}$$

where $\mu_i^{\Pi 0}$ is the ideal gas fugacity of $i$ component at $P^0$=1 bar and at the system temperature.

To equate chemical potentials for equilibrium calculation between a fluid and hydrate phase, it is convenient to represent the chemical potential of empty hydrate in reference to ideal gas fugacity at 1 bar and system temperature.

$$\mu_W^{EH} = \mu_W^{\Pi 0} + RT\,ln(\,f_{pureW}^{EH}\,)$$

$$= \mu_W^{\Pi 0} + RT\,ln[\,P_W^{satEH}\,\phi_W^{satEH}\,] + V_W^{satEH}\,[\,P - P_W^{satEH}\,] \tag{5}$$

This relation requires the vapor pressure of the empty hydrate, $P_W^{satEH}$ and $V_W^{satEH}$. For the latter the literature correlation of Avlontis [8] was used. The vapor pressure of hypothetical empty hydrate was calculated by Sloan et al. [1] from calculation of hydrate-fluid hydrocarbon phase equilibria below freezing temperature of water. For structure I, the vapor pressure can be represented by

$$ln[\,P_W^{satEH}\,/\,atm\,] = 17.440 - 6003.9\,/[\,T\,/\,K\,] \tag{6}$$

From eqn (2) and (5) we have for the residual chemical potential of water in hydrates,

$$\mu_W^H - \mu_W^{\Pi 0} = RT\sum_j \nu_j\,ln[\,1 - C_{i,j}\,f_i^{\Pi}\,/(\,1 + C_{i,j}\,f_i^{\Pi}\,)]$$

$$+ RT\,ln[\,P_W^{satEH}\,\phi_W^{satEH}\,] + V_W^{satEH}\,[\,P - P_W^{satEH}\,] \tag{7}$$

For computation, $\mu_W^{\Pi}$ is also expressed in reference to ideal gas fugacity at 1 bar and system temperature so that eqn (1) is written as,

$$\mu_W^{\Pi} - \mu_W^{\Pi 0} = \mu_W^H - \mu_W^{\Pi 0} \tag{8}$$

The equality condition of fugacity of guest molecules is embedded in the relation. For fluid phase equilibria not involving hydrate phase,

$$\mu_i^{\Pi(1)} = \mu_i^{\Pi(2)} \tag{9}$$

where $\Pi(1)$ and $\Pi(2)$ are two fluid phases. For phase equilibria involving ice,

$$\mu_W^{\Pi} - \mu_W^{\Pi 0} = \mu_W^{I} - \mu_W^{\Pi 0} \tag{10}$$

$$\mu_W^{I} - \mu_W^{\Pi 0} = RT \ln[ P_W^{satI} \phi_W^{satI} ] + V_W^{satI} [ P - P_W^{satI} ] \tag{11}$$

A three-phase equilibrium involving hydrates is defined by the simultaneous solution of eqn (8) with either (9) or (10). Working equations are found in published works [3-6] and are summarized [2].

**EXPERIMENTAL**

All the experiments were performed using the apparatus shown in Figure 1. Two high-pressure view cells were used. A smaller cell was a variable volume view cell for adjustment of the system pressure. An insertion-type density transducer (model 7826) by Solatron was installed in the larger view cell. Temperature was measured inside the larger cell by the same transducer. Its accuracy was claimed to be less than $\pm 1$ kg/m$^3$ in density and $\pm 0.05$K in temperature. To enhance mixing, an external circulation loop was installed to circulate aqueous phase by a high-precision metering pump. The cells and the circulation loop were immersed in a temperature-controlled bath. Temperature of the bath was measured by Cole Palmer (model 8436-00) thermometer with 0.01K resolution. Valcom (model VPRT-350K) pressure gauge with the claimed accuracy of 0.06 MPa was used after calibration against a Heise gauge.

In measuring three-phase equilibria, degassed water was charged into the cell. Then methane gas was introduced. The system was cooled to about 3-4K below the anticipated hydrate-forming temperature. Once the hydrates were formed, they were allowed to decompose by raising the temperature slowly. Near the complete

decomposition by visual inspection, the system was maintained at the temperature for 8 hours. When no pressure change was detected, the condition was taken as the equilibrium condition. Subsequently, a different pressure was selected, and the procedure was repeated to obtain the incipient hydrate formation temperature.

In two phase equilibrium measurements, solubility of methane in aqueous phase was analyzed by sampling the fluid in the sampling loop and by expansion into the pre-calibrated chamber. Degassed water was charged into the cell until most of the cell was filled with solution. After methane in the view cell was completely changed to hydrate by subcooling, the system was maintained at a given temperature and pressure and was monitored for more than a day. With no detectable pressure change, small amounts of aqueous liquid phase were introduced into the evacuated sampling loop with a calibrated volume. The dissolved methane molecules in the sample were expanded in the expansion chamber whose volume was determined precisely using methane PVT measurements. A pressure transducer (Sensys, 0-30 psia, 0.25%) was used to measure the pressure of the expansion chamber. Amount of dissolved fluid was determined using the PVT relation. The accuracy in mole fraction measurements was estimated to be less than 5.2%. To test the procedure, the solubility of methane in water were determined and compared with literature values.


**RESULTS AND DISCUSSION**

To test the reliability of the present experimental study, three phase equilibria and solubility of methane in water were measured and compared with literature values. Experimental measurements are tabulated in Table 1 and 2. Comparisons with literature value are graphically demonstrated in Figs. 2 and 3. Absolute average deviation (AAD)

error of present dissociation pressure with best-fitted literature values was 2.1% for H-$L_W$-$V_{CH4}$. This value is comparable with AAD fitting error of literature value (2.0%). For solubility of methane in water, AAD error of measured values with best-fitted value was 6.6% and that of literature value was 4.4%. Estimated errors were presented in the experimental section. Present experimental solubility was found to be in good agreements with other experimental data within a maximum deviation of $1.7 \times 10^{-4}$ in mole fraction.

For the calculation of phase equilibria, the lattice fluid equation of state of You et al. [3, 4] and Lee et al. [5, 6] was used extensively. This equation of state uses two temperature-dependent molecular parameters representing segment number and segment interaction energy for physical interactions of each pure species. Hydrogen-bonding energy and entropy for water was proposed by Luck [10] and adjusted to give better results. The adjusted hydrogen-bonding free energy and entropy were –44.0 *kJ/mol* and –117 *J/mol-K* for temperature range of 240-295 K. Physical parameters for water were determined from saturated liquid density and vapor pressure. Below the freezing point of water, vapor pressure of subcooled liquid in Perry's handbook [11] were used for parameter determination. For ice the vapor pressure and density are needed. The vapor pressure of ice was from Perry's handbook and the density was from Avlontis [8]. In determination of methane parameters, pure component parameters from liquid, vapor density and vapor pressure of methane were extrapolated to hydrate-forming temperature and slightly adjusted for better results of supercritical gas density.

The binary interaction energy parameter was fitted to data and represented as a function of temperature as $k_{ij}= 1.39\text{-}4.83 \times 10^{-3} \times T$. Calculated results are compared with data and shown in Fig. 3. The Langmuir constants A and B in eqn (3) were fitted to

available three phase equilibrium data. For methane they were 18.254 and -0.068/K for smaller cavities and 8.711 and –0.031/K for larger cavities respectively.

Calculated results of three phase equilibria were demonstrated in Fig. 2 and Table 4. For the calculation of H-$L_W$-$V_{CH4}$ equilibria, most other investigators used EOS approach for calculation of vapor phase fugacity. However, for chemical potential in liquid phase, pure water is assumed and the following relation was used.

$$\Delta\mu_w^{H\Pi} = \Delta\mu_w^{H\Pi}(T_0,P_0) + \int_{T_0}^{T}(\Delta H_w^{H\Pi}/RT^2)dT + \int_{P_0}^{P}(\Delta V_w^{H\Pi}/RT)dP \qquad (12)$$

Sloan [1] used Peng-Robinson or Soave-Redlich-Kwong EOS. Present calculation showed good results for all phase equilibria in hydrate-forming temperature range. It should be noted that a jump of dissociation pressure that was present in Sloan's calculation is not observed at lower quadruple point temperature. It can be explained by the fact that Sloan had fixed quadruple point temperature at 273.15K as Lundgaard and Mollerup[12] pointed out.

Calculated methane solubility in water for $L_W$-$V_{CH4}$ equilibria are compared with data of Knapp et al. [9] in Fig. 3 and errors are summarized in Table 5. Solubility error of water in methane-rich phase is larger compared with that of methane in water-rich phase. Both solubilities of water in methane-rich phase and of methane in water-rich phase were calculated with a single binary parameter.

The solubility data of methane at 273K and 278K in H-$L_W$ equilibria were obtained in this work and are listed in Table 6 and showed in Fig. 4. The absolute average deviation between present experimental and predicted values for this system is 3.4%. This is well within the experimental accuracy. Above the three-phase equilibrium pressure, present solubility slowly decreases with pressure. Handa's calculation [13] shows similar trends.

Data on two phase equilibria of $H-V_{CH4}$ was known to be difficult to measure due to its metastability and low concentrations of water [1]. The only available data to authors was measurements by Aoyagi et al. [14]. The result of present calculation for $H-V_{CH4}$ equilibria was compared with data of Aoyagi et al. and errors are also summarized in Fig. 5 and Table 5. Ng and Robinson [15] calculated $H-V_{CH4}$ equilibria with various hydrate-forming gases. With the fugacity of empty hydrate as a function of temperature and pressure, Ng and Robinson semi-empirically predicted $H-V_{CH4}$ equilibria with absolute deviation of 2.8%. The absolute average deviation of present calculation is 8.3%. This value is larger than semi-empirical calculation by Ng and Robinson but much lesser than 23.5% of Sloan's calculation[1].

**CONCLUSION**

Dissociation pressures of $H-L_W-V_{CH4}$ and methane solubility in $H-L_W$ equilibria were measured for water-methane mixture. Estimated experimental accuracy was 0.06 MPa in pressure, 0.05K in temperature and 5.2% in composition. A variable volume view cell was used with a magnetic stirrer inside. Concentrations of methane in aqueous phase were determined by expanding dissolved gas from external sampling loop.

The lattice fluid equation of state by present authors was used consistently for fluid phases in the calculation of two and three phase equilibria. The Langmuir constants in the van der Waals and Platteeuw model for hydrates and hydrogen-bonding free energy of water were fitted to data. Various two and three phase equilibria of $L_W-V_{CH4}$, $H-L_W-V_{CH4}$, $H-I-V_{CH4}$, $H-L_W$, $H-V_{CH4}$ were predicted with a single binary interaction parameter. Good agreements between observed and calculated results were obtained except for water contents in methane-rich phase of $L_W-V_{CH4}$.

**ACKNOWLEDGEMENT**

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Table 1. Experimental dissociation pressures of methane hydrate in H-$L_W$-$V_{CH4}$ equilibria

| Temperature / K | Experimental pressure / MPa | Temperature / K | Experimental pressure / MPa |
|---|---|---|---|
| 276.5 | 3.68 | 283.0 | 7.13 |
| 278.5 | 4.19 | 283.8 | 7.73 |
| 279.7 | 4.90 | 284.5 | 8.33 |
| 281.3 | 6.07 | 285.8 | 9.55 |
| 282.2 | 6.55 | 286.3 | 9.66 |

Table 2. Experimental mole fraction of methane in aqueous phase in $L_W$–$V_{CH4}$ equilibria at 298.15 K

| Temperature / K | Pressure / MPa | $x_{CH4} \times 10^3$ | Temperature / K | Pressure / MPa | $x_{CH4} \times 10^3$ |
|---|---|---|---|---|---|
| 298.1 | 2.33 | 0.684 | 298.1 | 7.82 | 1.49 |
| 298.1 | 4.11 | 0.894 | 298.1 | 8.00 | 1.66 |
| 298.1 | 4.40 | 1.16 | 298.1 | 8.18 | 1.45 |
| 298.1 | 4.88 | 0.988 | 298.2 | 8.40 | 1.74 |
| 298.1 | 5.65 | 1.30 | 298.1 | 8.75 | 1.53 |
| 298.1 | 6.01 | 1.26 | 298.1 | 9.56 | 1.93 |
| 298.1 | 6.61 | 1.46 | 298.1 | 11.68 | 2.10 |
| 298.1 | 6.72 | 1.31 | 298.1 | 11.84 | 2.03 |
| 298.1 | 7.39 | 1.43 | 298.1 | 12.68 | 2.06 |
| 298.2 | 7.67 | 1.62 | | | |

Table 3. Pure parameters for Equation of state [3-6]

|  | $\varepsilon_a$ | $\varepsilon_b$ | $\varepsilon_c$ | $r_a$ | $r_b$ | $r_c$ |
|---|---|---|---|---|---|---|
| $H_2O$ | 170.178 | 2.846 | 5.702 | 1.802 | 0.000 | -0.001 |
| $CH_4$ | 53.542 | 0.016 | -0.103 | 3.911 | 0.003 | 0.002 |

$$\varepsilon_{ii}\,/\,k = \varepsilon_a + \varepsilon_b(\,T - 273.15\,) + \varepsilon_c\,[\,T\,ln(\,273.15\,/\,T\,) + (\,T - 273.15\,)]$$

$$r_i\ = r_a + r_b(\,T - 273.15\,) + r_c\,[\,T\,ln(\,273.15\,/\,T\,) + (\,T - 273.15\,)]$$

Table 4. Comparison of experimental and calculated dissociation pressure of methane hydrate in three phase equilibria

| Phase | No. of pts. | Present calculation [a] | Calculation by Sloan [1] [a] | T range [K] | P range [MPa] | Reference |
|---|---|---|---|---|---|---|
| $H$-$I$-$V_{CH4}$ | 5 | 2.6 | 1.3 | 262.4-270.9 | 0.18-0.24 | [1] |
| $H$-$L_W$-$V_{CH4}$ | 55 | 2.7 | 5.6 | 273.2-294.3 | 0.27-28.60 | [1] This work |

[a]AADP [%]

Table 5. Comparison of experimental and calculated composition of two phase equilibria

| Phase | No. of pts. | AADP [%] | T range [K] | P range [MPa] | Reference | Data type |
|---|---|---|---|---|---|---|
| $L_W$-$V_{CH4}$ | 47 | 4.6 | 298.2 | 1.1-16.8 | [9], This work | a |
| $L_W$-$V_{CH4}$ | 5 | 26.6 | 298.2 | 2.4-12.2 | [9] | b |
| H-$L_W$ | 20 | 3.4 | 273.1-278.2 | 5.1-19.4 | This work | a |
| H-$V_{CH4}$ | 12 | 8.3 | 240.0-270.0 | 3.5-10.3 | [14] | b |

[a] Mole fraction of methane in water. [b] Mole fraction of water in methane-rich phase.

Table 6. Experimental mole fraction of methane in aqueous phase in H-$L_W$ equilibria

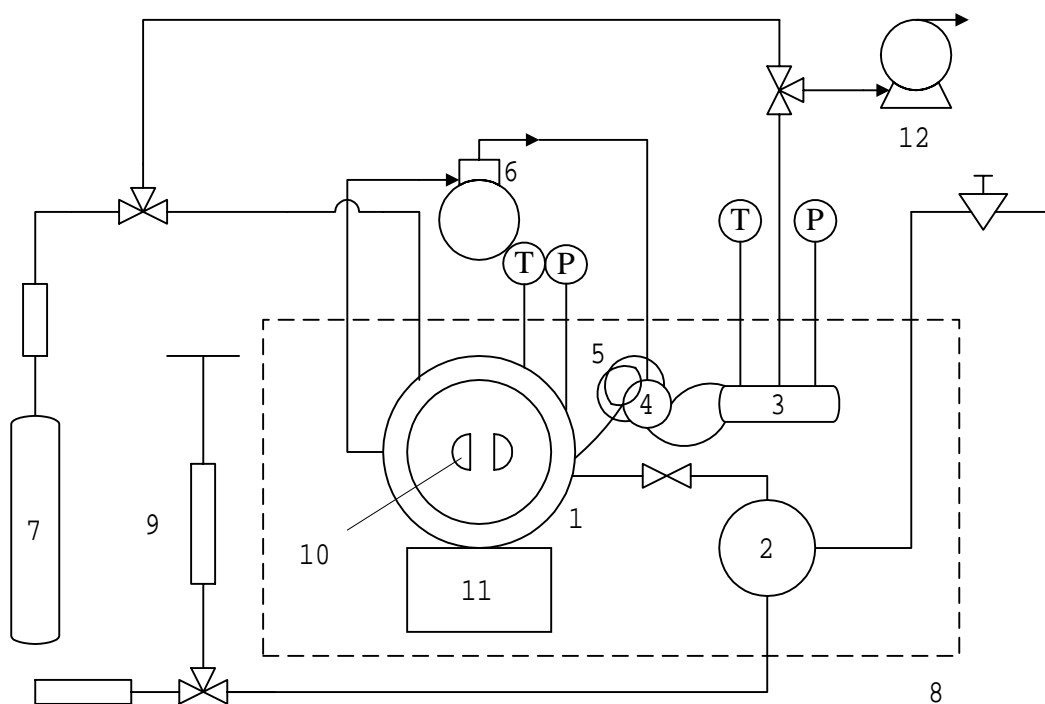| Temperature / K | Pressure / MPa | $x_{CH4} \times 10^3$ | Temperature / K | Pressure / MPa | $x_{CH4} \times 10^3$ |
|---|---|---|---|---|---|
| 278.1 | 5.79 | 1.14 | 278.1 | 19.35 | 0.960 |
| 278.1 | 8.12 | 1.03 | 273.1 | 4.98 | 0.775 |
| 278.2 | 8.89 | 1.04 | 273.1 | 5.20 | 0.751 |
| 278.2 | 10.44 | 1.13 | 273.1 | 7.85 | 0.770 |
| 278.2 | 11.18 | 1.01 | 273.1 | 8.42 | 0.776 |
| 278.1 | 11.53 | 1.06 | 273.1 | 11.63 | 0.763 |
| 278.2 | 13.76 | 1.06 | 273.1 | 12.28 | 0.752 |
| 278.1 | 16.02 | 1.00 | 273.1 | 13.50 | 0.807 |
| 278.1 | 16.54 | 0.953 | 273.1 | 14.81 | 0.765 |
| 278.1 | 19.29 | 0.954 | | | |

Figure captions

Figure 1. Experimental apparatus; (1)equilibrium cell; (2)variable volume cell; (3)expansion cell; (4)sampling valve; (5)sampling loop; (6)precision metering pump; (7)methane bomb; (8)water bath; (9)pressure generator; (10)density transducer; (11)magnetic stirrer; (12)vacuum pump
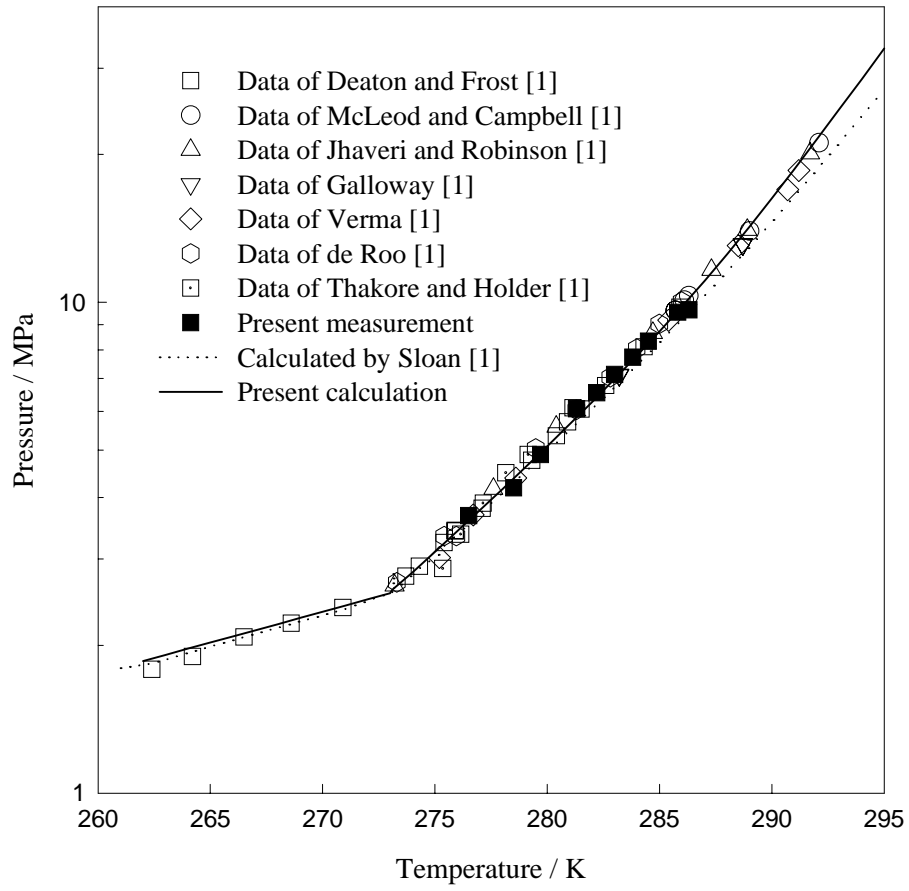
Figure 2. Comparison of experimental and calculated dissociation pressure of methane hydrate in three phase equilibria

Figure 3. Comparison of experimental and calculated solubility of methane in water and water in methane-rich phase of $L_W$-$V_{CH4}$ equilibria at 298.15 K

Figure 4. Comparison of experimental and calculated solubility of methane in water in H-$L_W$ equilibria at 278K and 273K

Figure 5. Comparison of experimental and calculated solubility of water in methane–rich phases of H-$V_{CH4}$ equilibria

Figure 1. Experimental apparatus; (1)equilibrium cell; (2)variable volume cell; (3)expansion cell; (4)sampling valve; (5)sampling loop; (6)precision metering pump; (7)methane bomb; (8)water bath; (9)pressure generator; (10)density transducer; (11)magnetic stirrer; (12)vacuum pump

Figure 2. Comparison of experimental and calculated dissociation pressure of methane hydrate in three phase equilibria
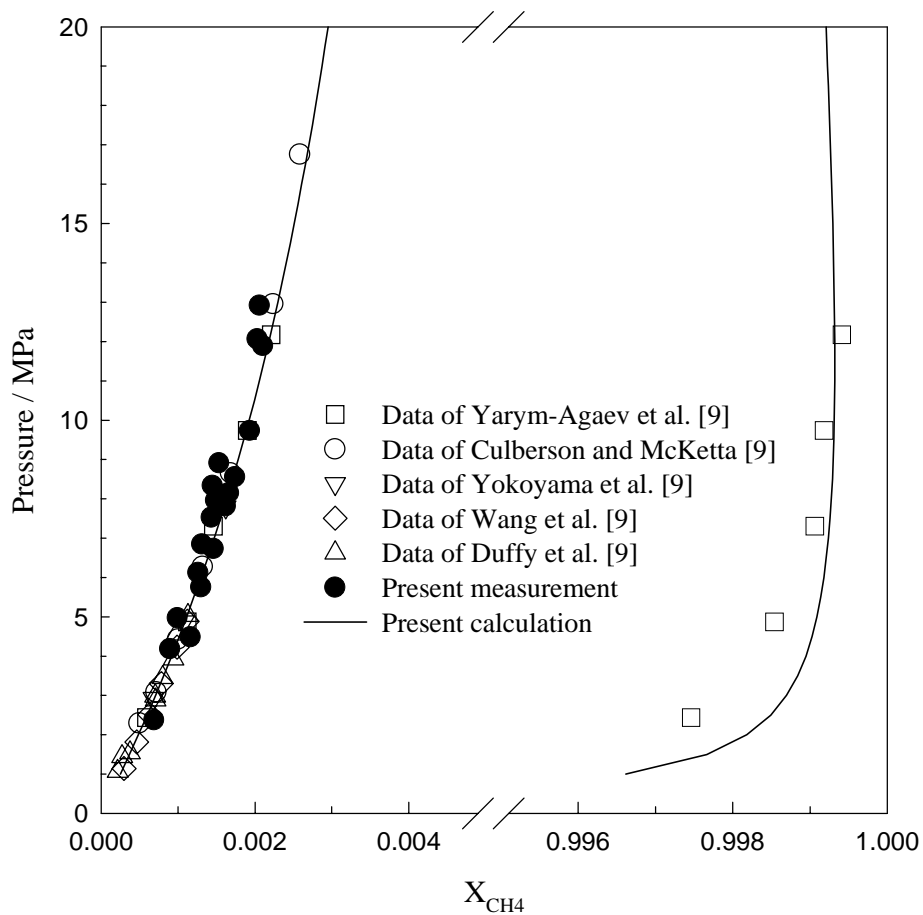
Figure 3. Comparison of experimental and calculated solubility of methane in water and water in methane-rich phase of $L_W$-$V_{CH4}$ equilibria at 298.15 K
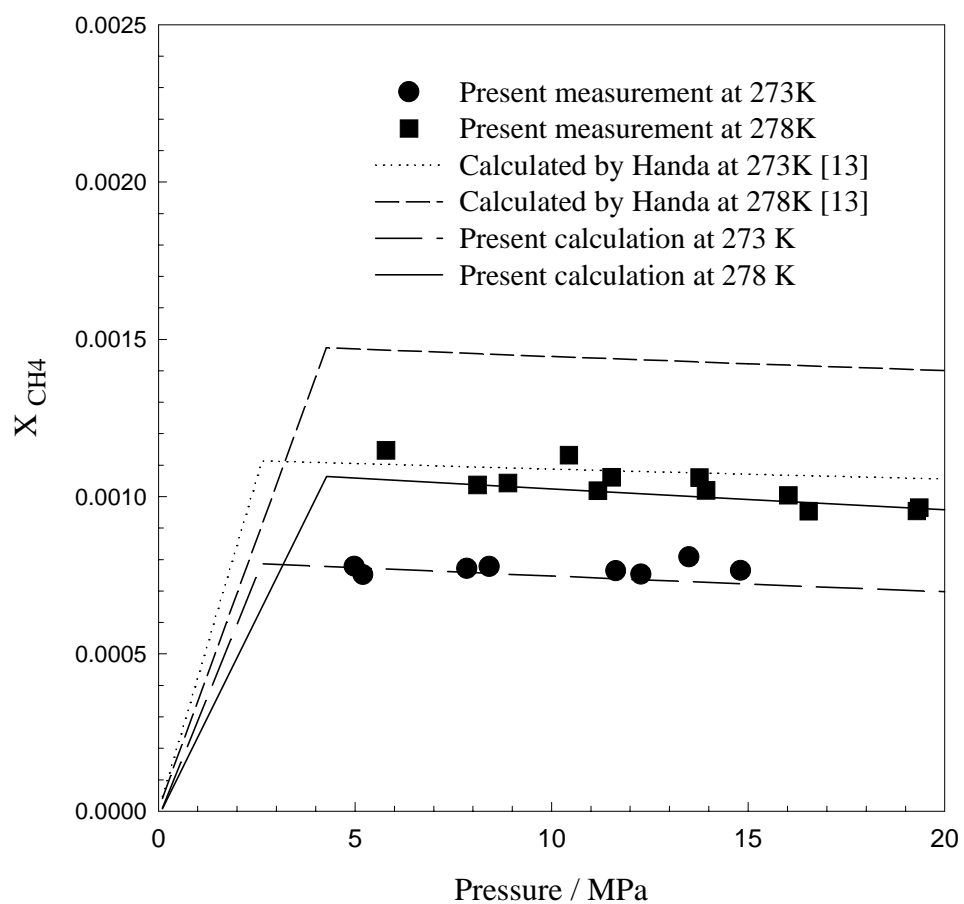
Figure 4. Comparison of experimental and calculated solubility of methane in water in H-L$_W$ equilibria at 278K and 273K
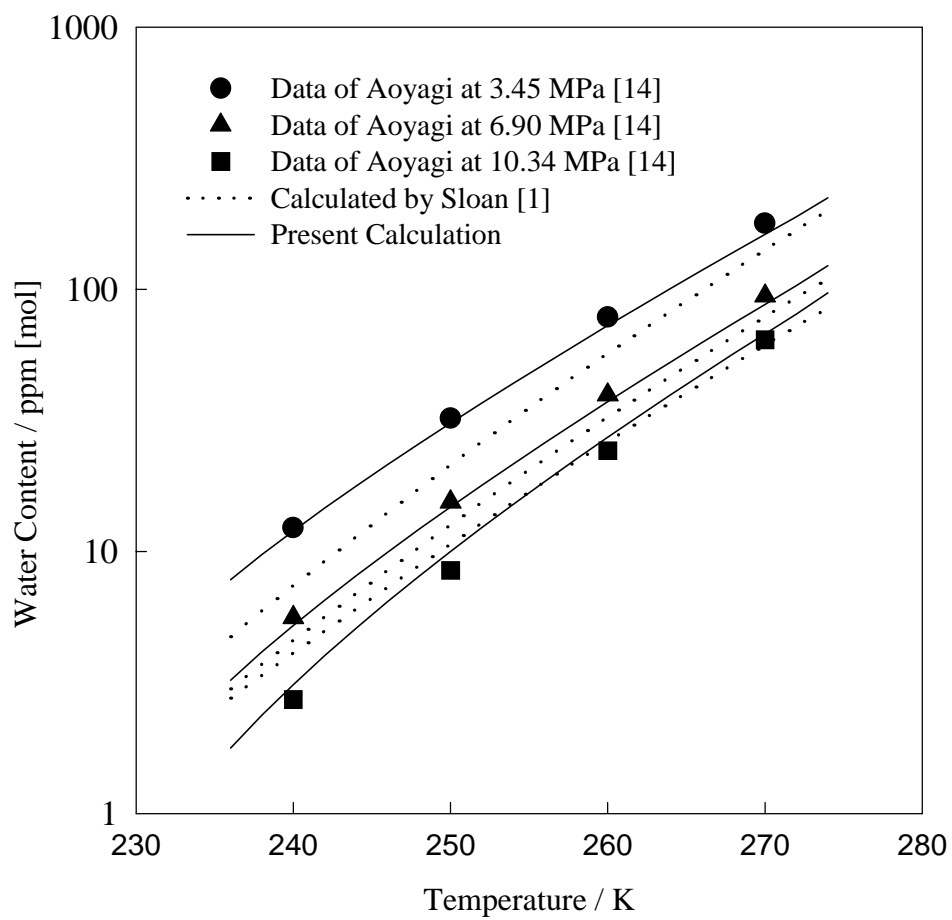
Figure 5. Comparison of experimental and calculated solubility of water in methane–rich phases of H-V$_{CH4}$ equilibria